2-ml aliquots were sealed in test tubes. For reactions with a moderate rate, where evaporation was not a problem, aliquots were pipeted directly from the reaction flask. For fast reactions, aliquots of each reactant were pipeted into opposite sides of a partition flask and allowed to equilibrate at the bath temperature, and the solutions were mixed by shaking so as to allow passage over the partition barrier.

The method of analysis consisted of quenching the aliquot in excess 5% aqueous potassium iodide solution, addition of a starch–iodine indicator to the yellow heterogeneous mixture, and titration of the resulting dark mixture to a pure yellow mixture with standard aqueous sodium thiosulfate.

Registry No.—Thallium triacetate, 2570-63-0.

Stereochemistry of the Radical Addition of Polyhalomethanes to Bicyclo[2.2.1]heptenyl Systems[1]

ADRIANE G. LUDWICK[2] AND J. C. MARTIN[3]

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801

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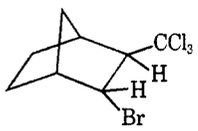
The radical addition of tribromofluoromethane to *endo*-2-substituted bicyclo[2.2.1]hept-5-enyl systems is shown to give both *trans* and *exo,cis* addition products, the relative amounts of each being dependent on the steric nature of the *endo*-2 substituent. The addition of tribromofluoromethane tobicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**10**) gives the *trans* adduct, *exo*-5-dibromofluoromethyl-*endo*-6-bromobicyclo[2.2.1]-heptane-*endo*-2,3-dicarboxylic anhydride (**11**), and the *exo,cis* adduct, *exo*-5-dibromofluoromethyl-*evo*-6-bromobicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (**12**), in yields of approximately 40 and 60%, respectively. The temperature-dependent ^{19}F nmr spectra of **12** reflect the steric hindrance to rotation of the dibromofluoromethyl group of this adduct, with peaks for each of the three conformers of this compound being resolved below −30°. The *trans* adduct gives only one peak in its ^{19}F spectrum. This difference is used to assign structures in a number of systems. The addition of tribromofluoromethane to bicyclo[2.2.1]hept-2-ene gives the *trans* adduct in greater than 95% yield.

Fawcett[4] suggested that the unreactivity of the bicyclo[2.2.1]hept-2-ene–bromotrichloromethane adduct toward potassium hydroxide, as observed by Kharasch and Friedlander,[5] supported a *trans* stereochemistry for this adduct. He argued that, since in this structure (**1**, *endo*-2-bromo-*exo*-3-trichloromethylbicyclo[2.2.1]-heptane) the hydrogen at carbon 3 would be *cis* to the



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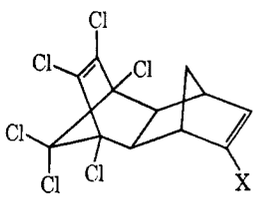
bromine, the preferred *trans* elimination would be prohibited. Evidence has since accumulated[6-11] to show that in systems with rigid structures *trans* elimination is not necessarily preferred.

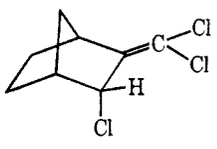
Dipole moment studies[12] of the adducts of chloroform and bromotrichloromethane with bicyclo[2.2.1]hept-2-ene have given some support for the formation of the *cis* adduct in the free-radical additions of these substrates.

The additions of carbon tetrachloride and of bromotrichloromethane to aldrin (**2a**) were found to give, respectively, the same products as the additions of chloroform to 6-chloroaldrin (**2b**) and 6-bromoaldrin (**2c**), respectively.[13] One can conclude from this observation that either *trans* addition is occurring in the carbon tetrachloride and bromotrichloromethane additions to **2a** and *cis* addition in the chloroform additions to **2b** and **2c** or that the reverse stereochemical result is correct.



2a, X = H
b, X = Cl
c, X = Br

Tobler and Foster[14] have presented evidence from nmr that the dehydrohalogenation product of the bicyclo[2.2.1]hept-2-ene–carbon tetrachloride adduct is 2-dichloromethylene-3-*endo*-chlorobicyclo[2.2.1]heptane (**3**). Hence, if one assumes that no rearrangement



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has occurred in the dehydrohalogenation of the bicyclo-[2.2.1]hept-2-ene–carbon tetrachloride adduct and that the trichloromethyl group is *exo*, then this must be the *trans* adduct.

During the course of this work, Osborn, VanAuken, and Trecker[15] reported the use of proton nmr spectros-

(1) Taken in part from the Ph.D. thesis of A. G. L., University of Illinois, 1967.
(2) National Institutes of Health Predoctoral Fellow, 1965–1967.
(3) Fellow of the Alfred P. Sloan Foundation, 1962–1966.
(4) F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).
(5) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).
(6) S. J. Cristol and N. L. Hause, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).
(7) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).
(8) H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).
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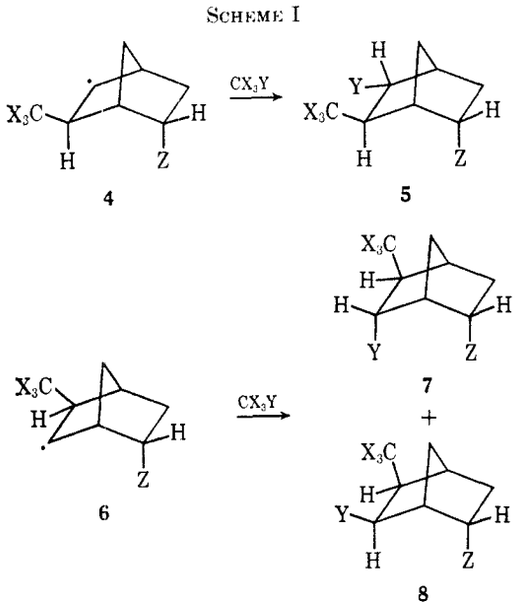
(11) J. K. Stille and F. M. Sonnenberg, *Tetrahedron Lett.*, 4587 (1966).
(12) V. A. Rolleri, *Dissertation Abstr.*, **19**, 960 (1958).
(13) D. I. Davies, *J. Chem. Soc.*, 3669 (1960).
(14) E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964).
(15) C. L. Osborn, T. V. VanAuken, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 5806 (1968).

copy to assign adduct structures in a demonstration that the radical addition of carbon tetrachloride to bicyclo[2.2.1]hept-2-ene gives a 73% yield of *trans* adduct and 4% *exo,cis* adduct. The radical addition of carbon tetrachloride to 5,5-dimethylbicyclo[2.2.1]hept-2-ene gives a 26% yield of *trans* adduct and 31% *exo,cis* adduct. Telomer formation accounts for the less than quantitative yields. A steric effect of the 5 substituent on the stereochemistry of the addition was postulated. Independently, and using a decidedly different approach, we have reach an analogous conclusion.

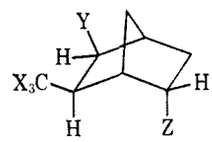
Results and Discussion

If the radical addition of polyhalomethanes to bicyclo[2.2.1]heptenyl systems is primarily *trans*, an *endo*-2 substituent in a bicyclo[2.2.1]hept-5-enyl system should affect the steric course of the addition. *exo* addition[16] of a trihalomethyl radical ($\cdot CX_3$) to *endo*-2-substituted bicyclo[2.2.1]hept-5-ene leads to radicals **4** and **6**. Abstraction of Y· in a *trans* sense from the polyhalomethane (CX_3Y) by radical **4** to give **5** should be relatively unaffected by the *endo*-2 substituent (Z). Abstraction of Y· in a *trans* sense from CX_3Y by radical **6** would be more subject to steric inhibition by nonbonded interactions between Z and the entering CX_3Y molecule. If the steric interaction between the CX_3 group at position **5** of **6** and a CX_3Y molecule entering from the *exo,cis* direction is of a similar magnitude, then *exo,cis* addition should begin to compete with *trans* addition to give both **7** and **8** (Scheme I).

SCHEME I



If the radical addition of polyhalomethanes to bicyclo[2.2.1]hept-2-ene were preferentially *exo,cis*, then it would appear that an *endo*-2 substituent in a bicyclo[2.2.1]hept-5-enyl system should have little effect on the steric course of the reaction. *exo,cis* abstraction of Y· from CX_2Y by radical **4** would lead to the *exo,cis* adduct **9** and the analogous reaction with radical **6** should lead to **8** alone.



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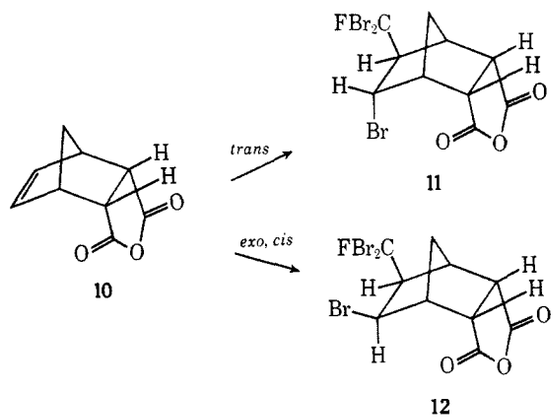
Addition to Bicyclo[2.2.1]-hept-5-ene-*endo*-2,3-dicarboxylic Anhydride (10).—The radical addition of tribromofluoromethane to bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**10**) can give only **11** (*trans* addition) and/or **12** (*exo,cis* addition) (Scheme II). The ambient temperature ^{19}F nmr spectrum of the

SCHEME II



product solution from the azobisisobutyronitrile (AIBN)-initiated addition of tribromofluoromethane to **10** indicates that this addition proceeds by both the *trans* and the *exo,cis* pathways. In the region of dibromofluoromethyl absorption, there is a doublet (J = 25 Hz) centered at 62.7 ppm (upfield from tribromofluoromethane) for one adduct and a broad absorption centered at 64.2 ppm for the other. Isolation of the second of these and study of the temperature dependence of its ^{19}F nmr absorption (Table I) allowed us to determine that it was the *exo,cis* adduct (**12**) and hence that the adduct giving the sharp doublet was the *trans* adduct (**11**).

At temperatures below −30° three peaks are seen for **12**. At −50° these are a doublet (J = 13.5 Hz) at 37.2 ppm (relative area, 1.0), a singlet at 55.2 ppm (area 1.9), and a doublet (J = 33.5 Hz) at 67.0 ppm (area 5.9). Coalescence of the high field doublet and the singlet peak is seen in the temperature range −30° to 10° to give a peak at 64.2 ppm at ≈30°. A value of 64 ppm is calculated from the weighted average of chemical shifts for the two peaks which coalesced to form this peak, assuming populations and chemical shifts for the two isomers to be temperature independent. The resulting peak coalesces with the remaining low field doublet at 37.1 ppm in the temperature range just below 125°. This gives a single peak at 61.6 ppm (125°), very near the 61 ppm calculated as above.

We interpret these observations in terms of the interconversions of three conformers, involving internal rotations of the CBr_2F group in the *exo,cis* adduct (**12**). The representations of these conformations seen in **A**,

(16) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699 701 (1967).

TABLE I

VARIATION OF PEAK POSITIONS WITH TEMPERATURE IN THE ^{19}F NMR OF *exo,cis* ADDUCTS OF $CFBr_3$ WITH **10**, **13a**, **13b**, AND **13c**

Temp, °C	Peak positions, ppm[a] 1[b]	2	3
150		60.9 ± 0.2 (broad)[c]	
125		61.6 ± 0.4 (broad)[c]	
100		Very broad[c,d]	
75		Very broad[d]	
50		64.8 ± 0.2 (broad)[d]	
Ambient	36.1 (broad)[c,e]		64.2 ± 0.2 (broad)[c]
	39.4 ± 0.2 (broad)[d]		65.1 ± 0.2 (broad)[d]
	Very broad[f]		66.1 ± 0.2 (broad)[f]
	39.7 ± 0.2 (broad)[g]		65.8 ± (0.2 (broad)[g]
10	38.0 (d)[c]		66.0 ± 0.4 (broad)[c]
	39.4 (d)[d]		66.0 ± 0.3 (broad)[d]
	40.6 (d)[f]		68.3 ± 0.3 (broad)[f]
	39.7 (d)[g]		66.1 ± 0.4 (broad)[g]
−10	37.6 (d)[c]	Very broad[c,d,f,g]	66.9 ± 0.2 (broad)[c]
	39.5 (d)[d]		67.2 ± 0.3 (broad)[d]
	40.7 (d)[f]		69.4 ± 0.2 (broad)[f]
	39.7 (d)[g]		68.7 ± 0.2 (broad)[g]
−30	37.7 (d)[c]	55.5 ± 0.2 (broad)[c]	67.3 ± 0.1 (d)[c]
	39.4 (d)[d]	Very broad[d]	68.1 ± 0.1 (d)[d]
	40.8 (d)[f]	58.0 ± 0.2 (broad)[f]	69.7 (d)[f]
	39.6 (d)[g]	56.6 ± 0.2 (broad)[g]	68.7 (d)[g]
−40	37.2 (d)[c]	55.0 (s)[c]	66.7 (d)[c]
−50	37.2 (d)[c]	55.2 (s)[c]	67.0 (d)[c]
	39.5 ± 0.1[d]	57.5 ± 0.1[d]	68.5 (d)[d]
	40.8 ± 0.1[f]	58.3 (s)[f]	69.9 (d)[f]
		56.7 ± 0.2[g]	68.9 ± 0.2[g]
−60	37.0 (d)[c]	55.1 (s)	66.8 (d)[c]
−70	37.0 (d)[c]	55.3 (s)	67.0 (d)[c]
−80	37.1 ± 0.1[c]	55.7 (s)	67.6 (d)[c]

[a] Peak positions are relative to $CFBr_3$. Solvents for these systems for given temperature ranges are as indicated in the Experimental Section, unless otherwise indicated. [b] Numbering (1, 2, and 3) designates absorptions observed at low temperatures for the three conformations of the CBr_2F group. [c] Adduct **12**. [d] Solvent was dimethylformamide. Corresponding absorption was not observed above spectrum noise (very broad) when solvent was d_6-acetone. [f] Adduct **16b**. [g] Adduct **16c**. Good spectra of this adduct could be obtained only to −30°.

B, and **C** of Figure 1 show qualitatively the deviations from the perfectly staggered conformations which result from nonbonded interactions between the substituents on the CBr_2F group and the *exo*-2-bromo substituent. A smaller interaction of the CBr_2F group with the proton at the *syn*-7 position was also considered in making these estimates of probable geometry from an inspection of molecular models.

The order of steric requirements for the substituents of the dibromofluoromethyl group is Br > F and the energetically most important interactions involving these substituents are probably those with the *exo*-6-bromo substituent. The interactions with the hydrogen at the *syn*-7 position can be considered of lesser importance. The order of stabilities **C** > **B** > **A** is then rationalized. We may use this order of predicted stabilities to make assignments for the three nmr peaks for **12** at low temperatures, using measured peak areas. The magnitude of coupling constants, J_{HF}, seen for the three conformer structures thus assigned provides confirmation for the assignments. The largest J_{HF} (33.5 Hz) is seen for conformer **C**, which has a dihedral angle near 180°. The smallest J_{HF} (near zero) is seen for conformer **B**, with a dihedral angle near 90°. Conformer **A**, with a dihedral angle of near 60°, has an intermediate value of J = 13.5 Hz. These values are in accord with those expected for these geometries from a comparison with literature values[17-20] for J_{HF} (vicinal) for compounds of known geometry.

The ^1H nmr spectrum of this adduct is also consistent with the assigned structure (**12**). The spectrum shows a four-line multiplet δ 4.54, J = 7.3 and 2.2 Hz, 1.00 H, which can be assigned to the absorption of proton 6. The larger coupling can be attributed[15,21-28] to coupling between an *endo* proton at position 6 and the *endo* proton at position 5 and the smaller constant to coupling between an *endo* proton at position 6 and the *anti* proton at position 7. The complex multiplets centered

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(21) P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964), and references cited therein.
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(23) E. A. Hill, *ibid.*, **31**, 20 (1966).
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(25) F. A. L. Anet, *Tetrahedron Lett.*, 3399 (1964).
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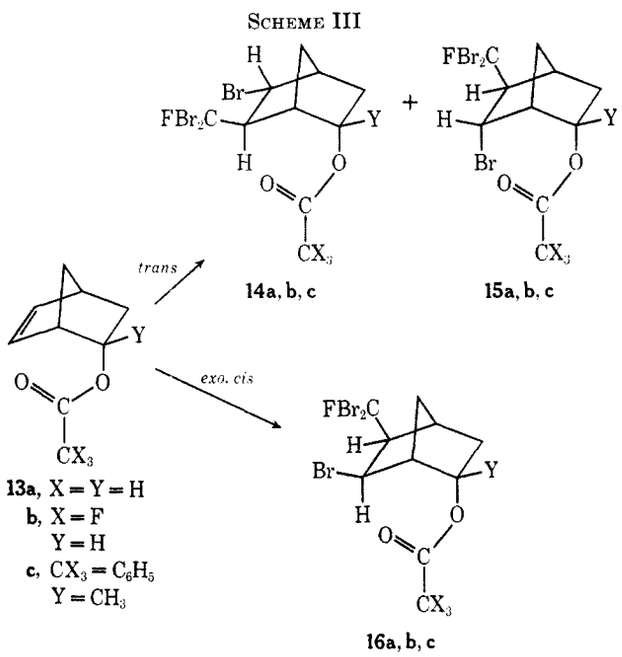
(27) F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *ibid.*, **89**, 4431 (1967).
(28) J. Paasivirta, *Suomen Kemistilehti*, **38B**, 130 (1965).

at about δ 3.94 (2.08 H) are assigned to the absorption of protons 2 and 3. The broad band centered at δ 3.32 (2.39 H) is assigned to include the absorptions of the bridgehead protons, 1 and 4, as well as half the absorption of proton 5. The absorption centered at about δ 2.97 (J = 7.4 Hz, 0.65 H), approximately 22 Hz upfield from the δ 3.32 absorption, can be attributed to the other half of the absorption of proton 5. This assignment is supported by an estimate (24 Hz) of the coupling constant between proton 5 and the fluorine atom vicinal to it from a weighted average of the coupling constants determined for conformers **A**, **B**, and **C** from the ^{19}F nmr low temperature spectra. The doublet at δ 2.65 (J = 11.2 Hz, 1.00 H) can be assigned to the absorption of proton 7, *anti* to the anhydride group. The other half of this AB pattern, at δ 2.00, can be assigned to the absorption for proton 7, *syn* to the anhydride group.

The ^1H nmr spectra of **12** at low temperatures (10 to −50°) show distinct changes with temperature in the regions assigned to protons 1, 4, 5, 6, and 7, in a manner consistent with the above interpretation of the ^{19}F nmr low temperature spectra of **12**.

Additions to *endo*-2-Substituted Bicyclo[2.2.1]hept-5-enyl Systems.—Applying the above steric rationale, the radical addition of tribromofluoromethane to *endo*-2-acetoxybicyclo[2.2.1]hept-5-ene (**13a**) would be expected to lead to two *trans* adducts (**14a** and **15a**) as well as an *exo,cis* adduct (**16a**) (Scheme III). If *trans*

SCHEME III



addition is preferred, then one would expect such addition of be inhibited by the *endo*-2-acetoxy group and hence the *exo,cis* adduct (**16a**) would be expected to form at the expense of the *trans* adduct (**15a**). Analogous products would be expected for **13b** and **13c**.

The AIBN-initiated additions of tribromofluoromethane to **13a** and **13b** proceed to give three adducts each. The room temperature ^{19}F nmr spectrum of the adducts of **31a** in the region of dibromofluoromethyl absorption shows an absorption pattern which can be attributed to two doublets of unequal intensity centered 61.5 and 61.9 ppm (J = 24 Hz). A broad absorption

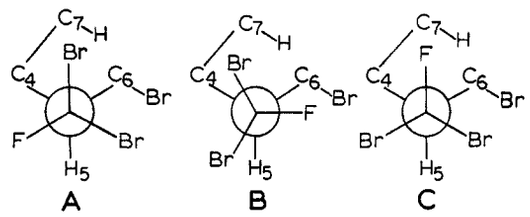


Figure 1.—Conformations of the CBr_2F group.

appears centered at 65.1 ppm and a smaller broad absorption centered at 39.4 ppm. Analogously, the room temperature ^{19}F nmr spectrum of the adducts of **13b** shows two doublets of unequal intensity centered at 62.8 and 63.5 ppm (J = 20.3 and 23.2 Hz, respectively) and a broad absorption at approximately 66.1 ppm. In the region of trifluoromethyl absorption (approximately 1000 Hz upfield from the dibromofluoromethyl region), the ^{19}F nmr spectrum shows three singlet absorptions with relative intensities of 1.00, 3.42 and 3.53, respectively.

The broad absorptions observed in the room temperature ^{19}F nmr spectra of the acetate and trifluoroacetate adducts were shown to be temperature dependent (Table I) in the manner shown for the *exo,cis* adduct in the anhydride system previously discussed. Hence it would appear reasonable to assign the broad absorptions to the *exo,cis* adducts (**16a** and **16b**) and the room temperature doublet absorptions to the *trans* adducts (**14a** and **14b**, **15a** and **15b**). As the *exo,cis* adducts (**16a** and **16b**) are expected to be formed at the expense of the *trans* adducts (**15a** and **15b**), it would also seem reasonable, if the assumption that the dibromofluoromethyl radical adds nearly equally rapidly to both positions 5 and 6 of **13a** and **13b** is valid, to assign the doublets of least intensity in the room temperature ^{19}F nmr spectra to **15a** and **15b**.

The room temperature ^1H nmr spectra of the tribromofluoromethane adducts of **13a** and **13b** were consistent with the above interpretation of the ^{19}F nmr spectra of these adducts (see Table II).

The AIBN-initiated addition of tribromofluoromethane to the benzoate (**13c**) gives predominantly two adducts. In the region of dibromofluoromethyl absorption, the ^{19}F nmr spectrum shows a doublet centered at 62.5 ppm ($J \approx 25$ Hz), a broad absorption centered at 65.8 ppm, and a smaller, barely perceptible, broad absorption centered at approximately 40 ppm. A considerably smaller amount of a second doublet was observed downfield from the major doublet centered at 62.5 ppm.

The broad absorptions in the ^{19}F nmr spectra exhibited the previously described temperature dependence (Table I). The broad absorptions in the room temperature ^{19}F nmr spectrum can be assigned to the *exo,cis* adduct (**16c**). It would then seem reasonable to assign the doublet at 62.5 ppm to the *trans* adduct (**14c**) and the remaining minor doublet to a small amount of the *trans* adduct (**15c**). The steric interaction of a tribromofluoromethane molecule with the *endo* benzoate group in the transition state for bromine atom abstraction leading to **15c** is shown to be larger than the corresponding interaction with the *exo*-5-substituted dibromofluoromethyl group and larger than that with the *endo* acetate or trifluoroacetate group by the larger amount of **16c** formed relative to **15c**.

TABLE II

ROOM TEMPERATURE ^{1}H NMR SPECTRA OF ADDUCTS

Adducts of	δ, ppm	J, Hz	Assignment
13a + Br_3FC	2.02, 2.06, 2.08		H_3C, **14a, 15a, 16a**
	4.55	7.5, 2	H-6, *endo*, **16a**[a]
	3.56	23.5, 6.0, 2	H-6, *endo*, **14a**, or H-5, *endo*, **15a**[a-c]
13b + Br_3FC	4.53	7, 2	H-6, *endo*, **16b**[a]
	3.27	6, 2	H-6, *endo*, **14b**[a,b,d]
13c + Br_3FC	1.69, 1.72		H_3C, **14c, 16c**
	4.5	7	H-6, *endo*, **16c**[a]
	3.5	6	H-6, *endo*, **14c**[a,b]
	4.2	m	H-5, *exo*, **14c** and
		m	H-6, *exo*, **15c**[e]
17a + Br_3FC	2.00		H_3C, **18a, 19a**
	5.20, 4.65	m	H-2, *endo*, **18a, 19a**
	4.11	m	H-5, *exo*, **18a**, and H-6, *exo*, **19a**[f]
17b + Br_3FC	5.54, 4.97	m	H-2, *endo*, **18b, 19b**
	4.17	m	H-5, *exo*, **18b**, and H-6, *exo*, **19b**[g]
20 + Br_3FC	4.13	m	H-2, *exo*, **21**
	2.63	24, 6, 2	H-3, *endo*, **21**[a,b]
20 + $BrCl_3C$	4.23	m	H-2, *exo*, **1**
13a + $BrCl_3C$	2.04, 2.09, 2.10		H_3C
	4.57	7.5	H-6, *endo*-2-acetoxy-*exo*-5-trichloromethyl-*exo*-6-bromobicyclo[2.2.1]-heptane[a,h]
	3.23	6.0	H-6, *endo*-2-acetoxy-*endo*-5-bromo-*exo*-trichloromethylbicyclo-[2.2.1]heptane[a,b]
17a + $BrCl_3C$	2.02		H_3C
	5.43, 4.73	m	CH_2—C(=O)—O—C(H)—
	4.20	m	H—C(Br)—

[a] References 15, 21–28. [b] Reference 23, in particular. [c] Superposition of other absorptions, preventing integration of the absorption of concern, did not allow a definite assignment. [d] The upfield half of this absorption (J_{HF}) was lost in other absorptions. [e] Relative areas of 4.5 and 4.2 absorptions are 1.00 and 0.86, respectively. [f] Relative areas of 5.20, 4.65, and 4.11 absorptions are 1.00, 0.95, and 2.04, respectively. [g] Relative areas of 5.54, 4.97, and 4.17 absorptions are 1.00, 1.00, and 2.00, respectively. [h] Relative area of 4.57 doublet to that of multiplet assignable to remaining absorptions of same type of proton in other components of mixture (1.00 to 1.54) can be used to infer relative amounts of *exo,cis* to *trans* addition. [i] Relative areas of 5.43, 3.74, and 4.20 absorptions are 1.12, 1.00, and 2.12, respectively.

Table II shows that the ^{1}H nmr spectra of the tribromofluoromethane–**13c** adducts support their ^{19}F nmr spectra interpretation.

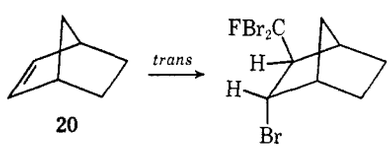
The relative ratios of *exo,cis* to *trans* addition observed in the reactions of tribromofluoromethane with *endo*-2-substituted (or *endo*-2,3-disubstituted) bicyclo[2.2.1]hept-5-enyl systems seem to parallel the steric requirements of the *endo*-substituted group (Table III). The preference for addition of a trihalomethyl radical at the 5 *vs.* the 6 position of a 2-substituted bicyclo[2.2.1]heptenyl system is insensitive to the *exo*-2 substituent. However, the presence of an *endo*-2 substituent evokes a preference of about 1.3 for addition at position 6 over addition at position 5. This might reflect a stabilization by the *endo*-2 substituents of the transition states leading to the trihalomethyl substituted radicals or a reversibility of the step adding the trihalomethyl radical to the double bond at position 5, where the chain transfer to position 6 is sterically retarded.

Additions to *exo*-2-Substituted Bicyclo[2.2.1]hept-5-enyl Systems.—If the above steric rationale is correct, the radical addition of tribromofluoromethane to *exo*-2-acetoxybicyclo[2.2.1]hept-5-ene (**17a**) and to the corresponding *exo* trifluoroacetate (**17b**) should proceed to give only the *trans* adducts (**18a**, **19a** and **18b**, **19b**, respectively) (Scheme IV). *exo,cis* addition should occur, if at all, only to a limited extent, since abstraction in a *trans* sense of a bromine atom from tribromofluoromethane by intermediate radicals would involve steric interaction primarily between the tribromofluoromethane molecule and the *endo*-2 proton.

The AIBN-initiated additions of tribromofluoromethane to the *exo* acetate (**17a**) and *exo* trifluoroacetate (**17b**) do, in fact, lead to the formation of only two adducts each.[29,30] The room temperature ^{19}F nmr spectrum of the *exo* acetate adducts shows two doublets of nearly equal intensity centered at 61.8 ppm (J = 22.4 Hz) and 63.1 ppm (J = 24.6 Hz). In the region of dibromofluoromethyl absorption, the room temperature ^{19}F nmr spectrum of the *exo* trifluoroacetate product solution shows two doublets of nearly equal intensity centered at 63.0 ppm (J = 22.0 Hz) and 64.4 ppm (J = 24.3 Hz). In neither spectrum, in the region of dibromofluoromethyl absorption, were broad absorptions attributable to *exo,cis* adducts observed above the spectrum noise.

The ^{1}H nmr spectra of the tribromofluoromethane adducts of **17a** and **17b** (Table II) also indicate two adducts formed in equivalent amounts for each system.

Addition to Bicyclo[2.2.1]hept-2-ene (**20**).—The above steric rationale suggests that the radical addition of tribromofluoromethane to **20** should give predominantly the *trans* adduct (**21**). The room temperature ^{19}F nmr spectrum of the product solution from the AIBN-initiated addition of tribromofluoromethane to **20** shows a doublet centered at 62.3 ppm (J = 24.35 Hz). No broad absorption of the sort expected for an *exo,cis* adduct was observed.



20 **21**

In the ^{19}F nmr spectrum of the above product solution at −50°, the doublet observed in the room temperature spectrum (62.3 ppm) has shifted upfield to 64.7 ppm (J = 25 Hz). In addition, the existence of a minor amount of a second adduct (corresponding to less than 3% of the total ^{19}F absorption) is shown by a doublet centered at 67.9 ppm (J = 35 Hz). Clearly,

(29) The ^{19}F and ^{1}H nmr spectra of the product solution from the AIBN-initiated addition of tribromofluoromethane to an *exo,endo* mixture of the acetates (**13a** and **17a**) confirmed the nonidentity of the ^{19}F doublet absorptions at 61.9 and 61.8 ppm and the methyl proton absorptions at δ 2.02 and 2.00.

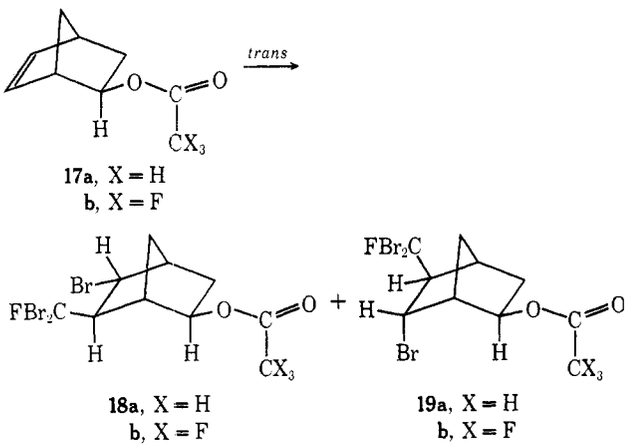
(30) The ^{19}F and ^{1}H nmr spectra of the product solution from the AIBN-initiated addition of tribromofluoromethane to an *exo,endo* mixture of the trifluoroacetates (**13b** and **17b**) were consistent with the assignments made to the *exo* trifluoroacetate adducts and the *endo* trifluoroacetate adducts.

TABLE III
RELATIVE AMOUNTS OF *trans* AND *exo,cis* ADDITION TO BICYCLO[2.2.1]HEPTENYL-TRIBROMOFLUOROMETHANE SYSTEMS

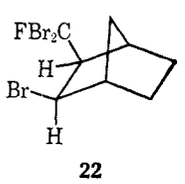
Bicyclo[2.2.1]heptenyl system[a]	Position of bromine atom substituent: *trans* 5	*trans* 6	*exo,cis*	Ratio of (*trans* 6 + *exo,cis*)/*trans* 5
endo acetate (**13a**)[b]	2.17	1.00	1.98	1.37
exo acetate (**17a**)	1.00 (or 0.95)	0.95 (or 1.00)		
endo trifluoroacetate (**13b**)	3.53 (or 3.42)	1.00	3.42 (or 3.53)	1.25 (or 1.32)
exo trifluoroacetate (**17b**)	1.00	1.00		
Benzoate (**13c**)	0.81[c]	0.05[c]	1.00	1.30
Anhydride (**10**)[d]	1.00		1.47	

[a] Values were obtained as indicated elsewhere in this paper unless otherwise noted. [b] Values were obtained from a fourfold sweep integration of a 500-cps sweep-width room temperature ^{19}F nmr spectrum in the region of dibromofluoromethyl absorption. Absorption 1 of the *exo,cis* adduct was not included in the integration but correction was made for it using the relative intensity values at −50° of absorptions 1, 2, and 3. [c] The *trans*-6 absorption was determined by planimeter integration of a 500-cps sweep-width room temperature ^{19}F nmr spectrum in the region of dibromofluoromethyl absorption to be 6% of the total *trans* adduct absorption. Using the value of total *trans* adduct absorption (0.86) relative to *exo,cis* absorption (determined as indicated elsewhere in this paper) the relative *trans*-5 and *trans*-6 values listed were calculated. [d] Values were obtained by assuming, from a visual inspection of the appropriate spectrum, that the intensities of the *trans* adduct absorption and absorption 3 of the *exo,cis* adduct at −50° were equivalent and then using the relative intensity values at −50° of absorptions 1, 2, and 3 to calculate the total intensity of the *exo,cis* adduct absorption.

SCHEME IV



this additional doublet observed at −50° can be assigned to conformation **C** of the *exo,cis* adduct (**22**)



22

(Figure 1), the absorptions for the other two conformations (**A** and **B**) not being visible above the spectrum noise. The corresponding broad absorptions of the room temperature ^{19}F nmr spectrum would also not be visible above the spectrum noise.

The ^1H nmr spectrum of the above product solution (Table II) is consistent with that expected for adduct **21**.

Bromotrichloromethane Additions.—The ^1H nmr spectra of the product solutions from the AIBN-initiated additions of bromotrichloromethane to **20**, **13a**, and **17a** are not subject to simple interpretation. Their patterns (Table II) are quite similar, however, to those of the ^1H nmr spectra of the product solutions from the corresponding radical additions of tribromofluoromethane. In particular, the proton of the bromomethylene group can be used to estimate relative amounts of *exo,cis* and *trans* adducts. These appear to be formed in ratios similar to those seen in the same systems for addition of tribromofluoromethane. Conclusions concerning the stereochemistry of additions of bromotrichloromethane to norbornenyl systems which are qualitatively similar to those which we derived for tribromofluoromethane addition are justified by ^1H nmr results.

Experimental Section

General Procedure for the AIBN-Initiated Addition of Tetrahalomethanes to 2-Substituted Bicyclo[2.2.1]hept-5-enyl Systems.—Reagents were thoroughly degassed and sealed in an nmr sample tube. The nmr tube was stored in the dark at Dry Ice temperature until needed, then heated to the reaction temperature. Nmr spectra were obtained on the Varian Associates Model A-56-60, A-60A, or HA-100 spectrometer before and after reaction. These reactions are summarized in Table IV. In all cases, the reaction time represents the minimum time for essentially complete reaction.

TABLE IV
AIBN-INITIATED ADDITION OF TETRAHALOMETHANE TO BICYCLO[2.2.1]HEPTENYL SYSTEMS AT 80°

CX_4	Olefin	Olefin, mmol	CX_4, mmol	AIBN, mmol	Reaction time, min
$CFBr_3$	**13a** and **17a**	1.506	5.9	0.033	5
$CFBr_3$	**17a**	1.522	5.9	0.039	5
$CFBr_3$	**13a**	1.454	5.9	0.033	5
$CFBr_3$	**13b** and **17b**	1.197	5.9	0.030	5
$CFBr_3$	**17b**	1.097	5.849	0.029	5
$CFBr_3$	**13b**	1.104	5.870	0.038	5
$CFBr_3$	**13c**	0.890	4.907	0.036	20
$CBrCl_3$	**20**	1.292	4.0	0.038	30
$CBrCl_3$	**13a** and **17a**	0.640	4.393	0.030	90
$CBrCl_3$	**17a**	0.300	4.342	0.030	30
$CBrCl_3$	**13a**	0.594	4.195	0.026	90

Addition of Tribromofluoromethane to Bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic Anhydride (10).—Anhydride **10** (0.722 mmol) in 0.5 ml of tribromofluoromethane containing AIBN (0.029 mmol) was heated for 35 min at 80°. Although the solution was homogeneous during this heating period, the resulting adducts, as the starting material, were poorly soluble in tribromofluoromethane at room temperature. The tribromofluoromethane was removed under reduced pressure and room temperature spectra were obtained in d_6-acetone.

Addition of Tribromofluoromethane to Bicyclo[2.2.1]hept-2-ene (20).—A solution of **20** (1.412 mmol) and of AIBN (0.030 mmol) in 0.40 ml of tribromofluoromethane in an nmr tube was allowed to react at room temperature. Spectra were obtained on the homogeneous reaction mixture.

Control Experiments.—Materials were placed in the nmr tube, thoroughly degassed, and the nmr tube was sealed. Spectra were obtained before and after reaction at 80°. Anhydride **10** was shown by nmr not to react with CCl_4 in 1 hr in the presence of 10% AIBN. Negligible reaction was seen for $CFBr_3$ in 1 hr in

the absence of AIBN. Bicyclo[2.2.1]hept-2-ene (**20**) reacted with $CFBr_3$ to the extent of 28% in 5 min in the absence of AIBN. A mixture of the *endo* (>70%) and *exo* acetates (**13a** and **17a**) was shown not to react with CCl_4 in 1.5 hr in the presence of 10% AIBN. This mixture did react with $CBrCl_3$ in 2.0 hr in the absence of AIBN (43%) and $CFBr_3$ in 5 min in the absence of AIBN (62%). No *endo* to *exo* acetate isomerization was observed during these reactions. A mixture of the *endo* and *exo* trifluoroacetates (**13b** and **17b**) was shown not to react in 20 min at 80° with either CCl_4 in the presence of 10% AIBN or $CFBr_3$ in the absence of AIBN. Negligible reaction was observed for the benzoate (**13c**) in 1 hr at 80° with either CCl_4 in the presence of 10% AIBN or $CFBr_3$ in the absence of AIBN.

Nmr Temperature Study of Adducts.—The Varian Associates Model A-56-60 spectrometer with variable temperature controller, Model V-6040, was used for all temperature work. All changes of spectra with temperature were shown to be reversible.

Bromobenzene solvent was washed with equivalent volumes of sulfuric acid and water, dried over sodium sulfate, and distilled, bp 154.0.[31] Pentamethylbenzene was recrystallized from 80% aqueous ethanol (approximately 7.3 g of hydrocarbon/120 ml of solvent), white leaflets, mp 53.0–54.0°.

Fluorine spectra were obtained of a solution of anhydride **12** (0.1203 g in 0.40 ml of d_6-acetone with tribromofluoromethane[32] as an internal standard) in a sealed nmr tube in the range from room temperature to −80°. The ^1H nmr spectra were obtained in the range from room temperature to −50°. A solution of **12** (0.1151 g), 0.40 ml of bromobenzene, and tribromofluoromethane (internal standard) was examined in the ^{19}F region in the range from room temperature to 150°. The anhydride was not completely soluble in the bromobenzene below 100°. A solution of 0.127 g of the anhydride and 0.42 g of pentamethylbenzene was studied over the range of 160 to 100°. Recovery of the anhydride established that it had not been destroyed in heating to 200°.

The tribromofluoromethane solution of the adducts of **13a** with tribromofluoromethane, in the sealed, degassed nmr tube used for the reaction, was studied by ^{19}F nmr in the range from −50 to 100°. Adducts of tribromofluoromethane with the *endo* trifluoroacetate (**13b**) and *endo* benzoate (**13c**) were studied analogously in the temperature range from −50° to room temperature.

The tribromofluoromethane solution of the adducts of bicyclo[2.2.1]hept-2-ene (**20**) with tribromofluoromethane in the sealed, degassed nmr tube used for reaction was studied in the ^{19}F nmr at room temperature and −50°.

Syntheses. A. Materials.—α-Acetoxyacrylonitrile was kindly supplied by Dr. John C. Little of Dow Chemical Co., Midland, Mich. [99.1% purity, bp 54° (10 mm)]. Azobisisobutyronitrile (AIBN) was recrystallized several times from 50% aqueous ethanol, mp 103.5–104.5°. Bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**10**) (Aldrich Chemical Co.) was recrystallized from benzene, mp 163–167°. Bicyclo[2.2.1]-hept-2-ene (**20**) (Aldrich Chemical Co.) was distilled, bp 94.0–96.0°. Bromotrichloromethane (Matheson Coleman and Bell) was distilled, bp 102.0–103.0°. This distillate was washed with an equivalent volume of water, dried over sodium sulfate, and distilled at reduced pressure to give a clear, colorless liquid, bp 42° (80 mm). It was stored in the dark.

Tribromofluoromethane was prepared according to the procedure of Birchall and Haszeldine[33] to give 40.9% (lit.[33] 65–75%) of a clear, pale yellow liquid, bp 105.0–108.0, $n^{23.5}D$ 1.5226 (lit.[33] bp 106–107°). Material was redistilled at reduced pressure using a 12 cm Vigreux column to give a clear, colorless liquid (34.3%), bp 46.5–47.0° (93 mm), $n^{23.5}D$ 1.5229. It was stored protected from light and moisture.

B. *exo*-5-Dibromofluoromethyl-*exo*-6-bromobicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic Anhydride (12).—A glass bomb was degassed and sealed with 0.9258 g of bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**10**) (0.005640 mol), 0.0253 g of AIBN (0.000154 mol), and 4.5 ml of tribromofluoromethane. The contents of the bomb were allowed to react for 1 hr at 80°, giving a clear, pale yellow solution. The bomb was cooled to room temperature in the dark and allowed to stand overnight. During this period, a white solid precipitated from solution. The tribromofluoromethane-insoluble material (1.72 g) was collected by suction filtration. Material soluble in tribromofluoromethane (1.33 g) was obtained by evaporating the solvent from the filtrate. Nmr spectra of these two fractions showed the insoluble material to be nearly entirely **12**. The soluble material was a mixture of **11** and **12**.

The tribromofluoromethane-insoluble material was recrystallized twice from carbon tetrachloride, using approximately 100 ml of carbon tetrachloride for 1.22 g of material, to give 1.05 g of short, white needles (0.00241 mol, 42.7%), mp 186.5–191.0°.

Anal. Calcd for $C_{10}H_8O_3Br_3F$: C, 27.61; H, 1.85. Found: C, 27.58; H, 1.83.

The ^1H nmr spectrum (in d_6-acetone) at room temperature was analyzed with the aid of a Varian spin decoupler, Model V-6085A.

A sample of **12** in d_6-acetone was recovered after spectra of the solution had been obtained at room temperature and −50°. The residue from the acetone solution was dried under reduced pressure at 40° over phosphorus pentoxide and identified from its infrared spectrum (Nujol mull) and elemental analysis as being identical with **12**.

C. *endo*-2-Acetoxybicyclo[2.2.1]hept-5-ene (13a).—The acetate was prepared according to the procedure of Winstein and Trifan.[34] The crude product was purified by distillations at reduced pressure to give a 12.3% yield of the acetate: bp 74.5° (12 mm); $n^{2.65}D$ 1.4658 [lit.[35] bp 72° (10 mm); $n^{25}D$ 1.4668]; nmr ($CDCl_3$), δ 6.12 (m 2.00, CH=CH), 5.25 (m, 0.78, CHOAc, *endo* acetate), 4.64 (m, 0.22, CHOAc, *exo* acetate), 3.13 and 2.83 (broad, 2.11), 1.54 μ (m, 7.70, including *exo* CH_2 at 2.02 and *endo* CH_2 at 1.95). The *endo* isomer of the acetate was obtained by preparative glpc separations of 25-μl aliquots of the *exo,endo* mixture on a 10 ft × 0.25 in. 20% diethylene glycol succinate column with Chromosorb P (60–80 mesh) as the solid support at 100–105°: nmr (CCl_4), δ 6.28, (m, 0.97, =CH), 5.93 (m, 1.00, =CH), 5.22 (m, 1.00, CHOAc), 3.11 (broad, 1.00, bridgehead CH), 2.82 (broad, 1.00, bridgehead CH), remaining upfield absorptions (m, 6.64, including CH_2 at 1.88).

D. *exo*-2-Acetoxybicyclo[2.2.1]hept-5-ene (17a).—The *exo* acetate was prepared by two[36,37] similar procedures. The crude acetate was distilled at reduced pressure and the resulting fractions analyzed on a 10 ft × 0.25 in. 15% Carbowax 20M column with Chromosorb W (60–80 mesh) as the solid support. Those fractions which predominantly showed peaks for the *exo*-norbornyl and -nortricyclyl acetates and only small amounts of other impurities were submitted to preparative glpc on the 15% Carbowax 20M column at 110–120°. The retention times for the *exo*-norbornyl and -nortricyclyl acetates were approximately 39.0 min and 56.6 min, respectively. However, injections were limited to a maximum of 25 μl because one of the trace impurities (perhaps the *endo*-norbornyl acetate) came off shortly after the *exo*-norbornyl acetate: nmr (CCl_4), δ 6.22 (m, 1.04, =CH), 5.98 (m, 0.87, =CH), 4.59 (m, 1.00, CHOAc), 2.84 (broad, 2.00, bridgehead CH), 1.54 (m, 6.91, including CH_2 at 1.97).

E. 2-Trifluoroacetoxybicyclo[2.2.1]hept-5-ene.—To a suspension of 3.40 g of sodium hydride (0.142 mol) in 100 ml of dry pentane was added, under nitrogen with stirring, a suspension of 15.00 g of 2-hydroxybicyclo[2.2.1]hept-5-ene (an *exo,endo* mixture) (Aldrich Chemical Co.) (0.136 mol). The reaction mixture was filtered under suction and the residue washed with dry pentane until the filtrate from the washing was clear and colorless The filtrates were concentrated under reduced pressure, giving 23.77 g of crude product. Distillation through a 12-cm Vigreux column gave 17.39 g of the trifluoroacetate (0.0844 mol, 62.1%), a clear, colorless liquid, bp 63.0–65.0° (21 mm), $n^{24.0}D$ 1.4085. This trifluoroacetate was redistilled to give 13.01 g (0.0631 mol, 46.4%) of clear, colorless material: bp 55.5° (15 mm); $n^{22.8}D$ 1.4088; nmr (CCl_4), δ 6.15 (m, 2.00, CH=CH), 5.43 (m, 0.72, $CHOCOCF_3$, *endo* ester), 4.84 (m, 0.26, $CHOCOCF_3$, *exo* ester), 3.26 (broad, 0.69), 2.93 (broad, 1.41), 2.13 (m, 0.97), 1.36 μ (m, 3.54); ^{19}F nmr (CCl_4) shows two singlets separated by approximately 1 Hz in the region of trifluoromethyl absorption.

The trifluoroacetate proved sensitive to heat as shown by its decomposition during distillation and its decomposition on a 10 ft × 0.25 in. 15% Carbowax 20M column with Chromosorb W (60–80 mesh) as the solid support at 105°.

(31) All boiling points are uncorrected. Melting points are corrected.

(32) Tribromofluoromethane, used as an internal standard in these experiments, absorbs 7.2 ppm downfield from trichlorofluoromethane.

(33) J. M. Birchall and R. N. Haszeldine, *J. Chem. Soc.*, **13** (1959).

(34) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1147 (1952).

(35) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(36) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962).

(37) S. J. Cristol, T. C. Morill, and R. A. Sanchez, *ibid.*, **88**, 3087 (1966).

Anal. Calcd for $C_9H_9O_2F_3$: C, 52.43; H, 4.40. Found: C, 53.48; H, 4.61.

The *endo* isomer of the trifluoroacetate (**13b**) was obtained by preparative glpc at 52–57° of 25-μl injections of the *exo,endo* mixture on a 10 ft × 0.25 in. 20% diethylene glycol succinate column with Chromosorb P (60–80 mesh) as the solid support.

Anal. Calcd for $C_9H_9O_2F_3$: C, 52.43; H, 4.40. Found: C, 52.94; H, 4.48.

This procedure also gave the *exo* isomer (**17b**).

Anal. Calcd for $C_9H_9O_2F_3$: C, 52.43; H, 4.40. Found: C, 53.03; H, 4.49.

F. *endo*-2-Hydroxy-*exo*-2-methylbicyclo[2.2.1]hept-5-ene.—Bicyclo[2.2.1]hept-5-en-2-one was prepared by oxidation of the corresponding carbinol by the method of Toivonen and Kaila[38] and through the hydrolysis of 2-cyano-2-acetoxybicyclo[2.2.1]-hept-5-ene by the method of Bartlett and Tate.[39] The latter precursor was prepared from α-acetoxyacrylonitrile and cyclopentadiene.[39] Addition of methylmagnesium iodide from 2.39 g of Mg (0.983 g-atom) and 5.6 ml of methyl iodide (0.090 mol) to this ketone was carried out by a modification of a method already described.[40] The Grignard reagent in 125 ml of dry diethyl ether was added dropwise with stirring to a solution of 6.03 g of bicyclo[2.2.1]hept-5-en-2-one (0.0558 mol) in 40 ml of anhydrous ether. The reaction mixture was stirred for 3 hr. To the reaction mixture was added 23 ml of saturated ammonium chloride solution. The reaction mixture was stirred an additional 15 min. The ether solution was dried over sodium sulfate, then distilled under reduced pressure using a short-path setup, giving 4.96 g (0.0399 mol, 71.5%) of the desired product, a clear and colorless liquid: bp 69.0° (15 mm); ir (10% CCl_4), 3596 (OH, m, sharp) and 3476 (w, broad) cm^{-1} [lit.[41,42] 3591 and 3610 (shoulder) for 0.005 *M* in CCl_4]; nmr (CCl_4), δ 6.21 (m, 2.00, CH=CH), 2.76 and 2.57 (broad, 2.17), remaining upfield absorptions (m, 8.36, including CH_2) at 1.43 [lit.[43] δ 6.26 (m, CH=CH), 2.82 and 2.63 (broad), 1.49 (s, CH_3)].

G. *endo*-2-Benzoyloxy-*exo*-2-methylbicyclo[2.2.1]hept-5-ene (13c).—To a solution of 1.00 g of *endo*-2-hydroxy-*exo*-2-methylbicyclo[2.2.1]hept-5-ene (0.00809 mol) in 20 ml of dry tetrahydrofuran approximately 5 ml of 1.6 *M* *n*-butyllithium (Foote Mineral Co.) (0.008 mol) was added dropwise with stirring. The solution was boiled under a nitrogen atmosphere for 25 hr. To the boiling solution was added dropwise 0.95 ml of freshly distilled benzoyl chloride (0.0083 mol). The reaction mixture was allowed to cool to room temperature and was filtered by suction. The tetrahydrofuran soluble residue was triturated with 20 ml of dry pentane and the resulting mixture filtered by means of suction. The filtrate was washed twice with 20-ml portions of water and dried over sodium sulfate. The pentane soluble residue was purified by chromatography, on silica gel with benzene eluent, to give the desired benzoate (1.16 g, 0.00508 mol, 63%), a pale yellow, clear, viscous liquid: nmr (CCl_4,) δ 7.60 (m, 4.95, aromatic CH), 6.11 (m, 1.95, CH=CH), 3.33 (broad, 1.00, bridgehead CH), 2.82 (broad, 1.03, bridgehead CH), 1.79 (s, 4.76, CH_3 plus some CH_2 absorption), 1.52 (m, 2.38, remaining CH_2 absorption).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.92; H, 7.04.

Registry No.—**12**, 21902-82-9; **13a**, 2890-95-1; **13b**, 21902-83-0; **13c**, 21927-68-4; **16a**, 21902-84-1; **16b**, 21902-85-2; **16c**, 21902-86-3; **17a**, 21902-87-4; **17b**, 21902-88-5.

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Substituent Effects in the Pyrolysis of Aryl *n*-Propyl Sulfoxides

DAVID W. EMERSON AND THOMAS J. KORNISKI

Division of Literature, Science, and Arts, The University of Michigan, Dearborn Campus, Dearborn, Michigan 48128

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The rates of propene formation in the thermal decomposition of phenyl *n*-propyl, *p*-chlorophenyl *n*-propyl, *p*-tolyl *n*-propyl, *p*-methoxyphenyl *n*-propyl, and *p*-nitrophenyl *n*-propyl sulfoxides in phenyl ether solution were measured. Propene formation obeys a first-order rate equation. Activation enthalpies and entropies were in the range of 25 to 28 kcal mol^{-1} and −11.5 to −16 cal deg^{-1} mol^{-1}, respectively. The electron-withdrawing *para* substituents chloro and nitro increased the rate, while methyl and methoxyl decreased the rate. The rates are correlated by a Hammett plot giving $\rho = 0.51$, $r = 0.995$. The results suggest a highly ordered, probably cyclic, transition state with a fractional negative charge developing on the sulfur-containing moiety and a fractional positive charge developing on the propyl group.

Sulfoxides with at least one alkyl group having a hydrogen atom attached to the β-carbon atom suffer thermal decomposition to yield alkenes[1] and sulfenic acids which can be trapped[1m] or which can decompose to form a variety of sulfur containing products.[1e] The mechanistic view that the reaction is a *cis* elimination involving a cyclic quasi five-membered-ring transition state has served to reconcile most of the experimental findings. The observation that unsymmetrical dialkyl sulfoxides preferentially eliminate alkenes derived from the alkyl groups more highly substituted on the α carbon atom[1f] prompted us to explore further aspects of the reaction. In view of the observation that a radical pair may be involved in the decomposition of some sulfoxides,[1a] it was deemed profitable to study the rates of decomposition of members of a series of *para*-substituted phenyl *n*-propyl sulfoxides in which propene was always eliminated so that the effects of substituents on the rates could be assessed. The results of this study are reported herein.

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Results and Discussion

Either radical intermediates or a transition state in which the carbon atom becoming separated from sulfur is developing some positive character could account for